GAS CHROMATOGRAPHY TECHNIQUES: APPLICATIONS IN THE AREA OF FUELS AND THEIR DERIVATIVES

A. Galtieri

Translation of "Tecniche gascromatografiche: applicazione nel settore dei combustibili e derivati," Revista di Combustibili, Vol. 25, 1971, pp. 417-427

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16. Abstract This paper presents a review of gas chromatography techniques, with special emphasis on analytical problems encountered in petroleum technology. Packed and capillary columns are discussed, including their resolution and efficiency; their characteristics are compared. Applications of gas chromatography to the analysis of mixtures of gases, hydrocarbons (aliphatic and aromatic), asphalts, and lead antiknock compounds are reviewed. The suitability of different types of columns, supports and coatings for different analyses is examined. Recent developments such as metastable helium detectors and electron capture detectors are discussed.

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GAS CHROMATOGRAPHY TECHNIQUES: APPLICATIONS IN THE AREA OF FUELS AND THEIR DERIVATIVES

A. Galtieri
Experimental Station for Fuels, San Donato Milanese

1. Introduction

It can be said that the whole of chemical science is based on analytical data of different types; it follows that analytical chemistry should be considered the foundation of all chemical sciences. It is thus in the best interests of every chemist to obtain thoroughly reliable analytical data and to be aware of the limitations and possibilities of the measuring instruments used.

Together with classical analytical methods, organic chemistry laboratories now use methods such as UV spectroscopy, IR in the visible range, nuclear magnetic resonance, mass spectroscopy, X-rays and gas chromatography. The so-called "black box" mentality has thus arisen, that is, the tendency to use analytical instruments without a good knowledge of their limitations, possibilities, and idiosyncrasies. Thus, the fact is usually neglected that an analytical instrument is a measuring device which determines a certain characteristic of the system by measuring it, so its result wil usually depend on how intelligently the measuring instrument has been used.

Analytical instruments are often compared with cars or television sets; this comparison is incorrect, since cars and TV sets can be defined as "yes/no" devices, functioning or not functioning. The main issue in these cases is in which of these two conditions they are.

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* Numbers in the margin indicate pagination in the foreign text.

It is hoped that analytical instruments may soon reach such a degree of perfection as to be effectively used as "yes/no" instruments.

Since the clever discovery by A.J.P. Martin that a substance in the gaseous phase can be chromatographed, this principle has been used in every area of chemistry, providing highly interesting results. The development of this techniques has been so productive both from theoretical and experimental viewpoints that interest in the potential applications of gaseous phase chromatography is constantly increasing.

The fact that in less than 20 years this techniques has provided such remarkable results is due to experts in various fields who have contributed to its development by contributing their experience.

This has been instrumental in eliminating much of the empirical aspect of gas chromatography, and now makes it possible to tackle any analytical problem with a high level of technical skill.

Gas chromatographic analysis is mainly known as a technique for the separation and determination of volatile compounds or compounds with a vapor tension high enough to permit them to be readily carried in the gaseous phase.

Recently there has been a steady broadening of the application of gas chromatography to include systems of very low volatility. In these cases, gas chromatography has also obtained brilliant results, jointly with or in place of other widespread analytical procedures, such as paper chromatography, thin-layer chromatography, or spectrophotometry.

It is known that gaseous-phase chromatography includes gas-liquid chromatography and gas-solid chromatography, depending on whether fractionation of a substance introduced into the chromatography column takes place through partition of the substance between the gaseous and the liquid phases -- the latter being on a solid support -- or through adsorption on an active solid support.

The order of elution of the various components depends on the respective partition coefficients or adsorption coefficients. The great possibility of separating the various compounds depends on the sizable differences in their interaction, with both the liquid phase and the surface of a solid. These are the reasons /418 for considering the gas chromatography column as the essential part of a gas chromatography apparatus, since it carries out the fractionation and thus allows separation of the various components of a mixture. This is pursued using two types of columns: packed columns and capillary columns.

2. Packed and Capillary Columns

Capillary gas chromatography is basically not different from classical gas chromatography with packed columns; it is actually an improvement of it which has led to formerly unattainable separation powers. In adsorption gas chromatography, the stationary phase is an active, solid, porous, granular material (Al_2O_3, SiO_2, activated charcoal), whose surface activity acts in a differential manner upon the individual components, slowing their passage through the column to different extents. The classical packed adsorption column is obtained by homogeneously filling a tube of 3-4 mm diameter and 1-2 m length (depending on the analytical problem) with the active material. There is no basic difference between adsorption chromatography with packed columns or with capillary packed columns; the difference is only in the smaller diameter of the capillary packed columns (0.2-0.4 mm).

The development of capillary packed columns seems to open a new, interesting field for high-temperature chromatography (solid supports with very low vapor tension), or for quick analyses.

In the case of gas-liquid partition chromatography, the active substance is a partition liquid called the stationary phase; in the case of packed columns, it is deposited on an inert, solid, porous, granular support, in order to increase the contact surface. This impregnated material is loaded into a tube, exactly as is done for adsorption columns, thus obtaining the classical packed partition column.

In capillary columns of this type, the stationary phase is deposed directly, in a layer about 0.001 mm thick, on the inside walls of a tube of 0.1-1 mm diameter (the most common diameter is around 0.25 mm), whose length may be 10-300 m, depending on the analytical problem.

The capillary tube may be made of plastic (nylon), glass, or metal (copper, stainless steel). The glass capillaries may be prepared in the laboratory using relatively simple equipment, developed by Desty. A glass tube 4-6 mm in diameter is submitted to constant traction in a small electric oven; it is then twisted, while heating, to make a compound spiral. The diameter of the capillary obtained in this manner depends both on the traction rate and on the temperature of the oven where the glass is softened.

Besides its brittleness, glass is difficult to coat with the stationary phase (due to its poor wettability), so appropriate surface treatments are required.

Stainless steel columns are frequently used; they can be cleaned and coated with the stationary phase with relative ease

and have a longer life than glass ones. Porcaro found 26.5 mg of extraneous material in a 200' column with an internal diameter of 0.50 mm, corresponding to a liquid film of about 0.32 µm.

Nollis recommends washing the columns with various solvents in the following order: pentane, methylene chloride, acetone, diethyl ether, and the solvent of the stationary phase.

The columns may be filled by two different procedures: static and dynamic. With the static method, first developed by Golay, the column is first completely filled with a solution of the stationary phase in a volatile solvent. A compressed gas is used to force the solution through the capillary. One end of the column is then closed, and it is passed slowly through a small oven, in whose hot zone the solvent will evaporate. The main advantage of the static method is that, since the solution fills the tube completely, the value of β (ratio between the volume of the gas phase V_G and that of the liquid phase V_L) may be calculated directly from the concentration of the liquid phase. For example, if a 1% solution by volume is used to coat a column of 125 µm diameter,

$$\beta = \frac{V_G}{V_L} = \frac{99}{1} = 99;$$

and since

$$\beta = \frac{r}{2\,df}$$

(d_f = film thickness)

$$d_f = \frac{r}{2\,\beta} = \frac{125}{198} = 0{,}63\ \mu m$$

It is evident that the value of β is independent of the column's diameter and depends only on the concentration of the coating.

Although this method permits better control of the thickness of the stationary phase film, in practice the dynamic method is used, due to its simplicity. Using the same setup, the solution is passed through the tube, and the solvent is then evaporated using a flow of inert gas such as argon, helium or nitrogen for several hours. Different film thicknesses may be obtained by changing either the percentage of the stationary phase in the solution or the rate of flow of the liquid.

The surface of the tubes presents secondary adsorption effects with the stationary phase and the substances to be examined. /419
These can be eliminated by adding certain organic compounds containing long inert chains bound to polar groups (partially esterified surface-active polyglycols). They neutralize the active centers and retain the stationary phase more strongly on the walls of the capillary. The amount of additive is about 0.1-0.2 for a 10% solution of the stationary phase.

3. Resolution of Chromatographic Column

The relative position of two consecutive peaks in a chromatogram is expressed by the relative retention or relative volatility (α):

$$\alpha = \frac{t^1 R_2}{t^1 R_1} = \frac{K_2}{K_1} = \frac{k_2}{k_1} \qquad (1)$$

where, by definition, $t^1R_2 > t^1R_1$. The relative volatility does not express the actual separation of the two consecutive peaks, since it does not take into account the area of the two peaks.

The actual separation that can be obtained between two adjacent peaks in a chromatogram doen on a given mixture is expressed by the "peak resolution":

$$R = \frac{t^1 R_2 - t^1 R_1}{\frac{1}{2}(W_{b1} + W_{b2})} = \frac{2\,\Delta t}{W_{b1} + W_{b2}} \qquad (2)$$

where t^1R_1 and t^1R_2 are the retention times of the two constituents, and W_{b1} and W_{b2} are the bases of the corresponding peaks. If the two peaks being examined are sufficiently cose that the two base halves can be assumed to be equal, the above expression may be simplified as follows:

$$R \simeq \frac{\Delta t}{W_{b2}}. \qquad (3)$$

It can be shown that for R = 1 the resolution of the two peaks of equal area is 98%, while for R = 1.5 the resolution is 99.7% ("base-line separation").

4. Efficiency of Chromatographic Column

Just as in distillation, a chromatographic column may be divided into theoretical plates; by convention, a theoretical plate is defined as the equivalent column length in which adsorption and desadsorption have reached an equilibrium given by the partition coefficient between the moving phase and the stationary phase.

The efficiency of a column is expressed by the number of theoretical plates (n):

$$n = 16\left(\frac{t_R}{W_b}\right)^2 = 5.54\left(\frac{t_R}{W_h}\right)^2. \qquad (4)$$

In gas chromatography practice it is preferable to replace (4) by an expression relating k, α and R. In this manner it is possible to calculate the number of theoretical plates required (n_{req}) in order to obtain the desired resolution (R) for a determined pair of components defined by α and k. This equation was derived by Purnell for two relatively close peaks:

$$n_{req} = 16\,R^2\left(\frac{\alpha}{\alpha-1}\right)^2\left(\frac{k+1}{k}\right)^2. \qquad (5)$$

In this equation, k refers to the second peak. If k is substituted by K/B, the equation may be written in the following form:

$$n_{req} = 16\,R^2\left(\frac{\alpha}{\alpha-1}\right)^2\left(\frac{\beta}{K}+1\right)^2. \qquad (6)$$

The maximum possible resolution (R*) for a given number of theoretical plates and the lowest relative volatility (α*) permitting a sufficient separation of two given components can also be calculated

$$R^* = \frac{\sqrt{n}}{4}\left(\frac{\alpha-1}{\alpha}\right)\left(\frac{k}{k+1}\right) \qquad (7a)$$

$$\alpha^* = \frac{\sqrt{n}}{\sqrt{n}-4\,R\left(\frac{k+1}{k}\right)}. \qquad (7b)$$

In order to compare the efficiency of different columns, it is preferable to use another characteristic magnitude, the HETP, which is obtained from the column's length and the number of plates:

$$HETP = \frac{L}{n}\,(L \text{ in mm}); \qquad (8)$$

HETP stands for "height equivalent to a theoretical plate." The smaller this equivalent height is, the larger the column's separation power will be. A low-efficiency column may have an HETP of a few centimeters, while an efficient column may have a HETP of 1 mm or less. HETP should remain constant for a given column without regard to the eluted substances. There is, however, a tendency for the HETP to decrease with the increase of the retention volume, and it may vary considerably with the solute's chemical nature. It is thus important to specify what the solute is when defining the plate number of the HETP.

This magnitude, which for simplicity's sake is called H, depends in turn on the linear velocity of the gas according to Van Deemter's classical equation, in which H is expressed as a function of the diffusion longitudinal to the mass transfer:

$$H = 2\lambda d_p + \frac{2\gamma D_G}{u} + \frac{8}{\pi^2}\frac{k}{(1+k)^2}\frac{d_f^2}{DL}u \qquad (9)$$

where u = average velocity of the transporting gas

λ = a measurement of packing irregularities

d_p = particle diameter /420

γ = winding factor

D_G = diffusion coefficient of the solute in the transporting gas

k = capacity ratio

d_f = thickness of stationary phase film

DL = diffusion constant of the solute in the liquid phase,

or, more simply,

$$H = A + B/U + Cu \qquad (10)$$

where u is the linear velocity of the carrier gas.

In this equation, A represents the contribution of eddy diffusion, and it depends particularly on the packing characteristics of the column and on the dimensions of the solid support. The term B/U is given by molecular diffusion, i.e., the diffusion of the sample's molecules into the elution gas. This magnitude will thus be a function of both the type of component and the type of elution gas. The term Cu includes the factors relating to the resistance to matter transfer.

The efficiency of a packed column is a function of a set of parameters relating to preparation, such as particle diameter,

packing, and liquid phase and relating to operation, such as temperature, pressure, and flow.

The approximate Dal Nogare-Chiu equation provides useful criteria for the preparation of columns that can perform separations with the best resolution and the highest possible efficiency:

$$\beta d_p \left(\frac{p_1}{p_o} + 1\right)\frac{1}{2} \cong 0.5$$

where β is the ratio of the total gas volume in the column V_G to the total volume of the stationary phase V_L at the column temperature where d_p is the diameter of the solid support particles, and p_1 and p_o are the entry and exit pressures of the column, respectively.

Based on this expression, the product of β and the diameter of the particles of the solid support must be about 0.5 in order to obtain the best resolution corresponding to the maximum efficiency. It can thus be assumed that the optimum separation can be obtained by following two different directions:

One is the use of a small, solid support with a low percentage of liquid phase, a relatively short column, and a small sample. In this manner a very high-efficiency, high-sensitivity, fast chromatogram is obtained. The other direction is to use relatively coarse material, high liquid phase concentrations, and relatively long columns; in this case, a high resolution is achieved with a low column efficiency, and the separation is carried out at a relatively slow rate with a decreased sensitivity. The first procedure is usually followed when separations must be carried out as fast as possible, as in automatic control processes; the second when particularly complex mixtures are analyzed.

5. Comparison of Packed and Capillary Columns

Let us now examine the basic differences between packed and capillary columns. A sizable difference can be observed in the value of β and in the column's permeability. The term β affects the number of theoretical plates needed for a given separation, while the permeability determines the duration of the analysis and establishes the practical limit of the column's length. The following parameters should thus be examined when comparing packed and capillary columns:

a) variations of the values of β and their effect on the column's characteristics;

b) the number of theoretical plates needed for a given separation;

c) permeability of the two types of columns and practical limits set by excessive entry pressure in order to maintain the required flow.

Next, the performance index and the various expressions regarding the concept of plate number should be considered. These terms have been examined to allow a direct comparison of the performance of packed and capillary columns.

In packed columns the value of β is relatively small: the values reported for commonly used columns are in the range 6-35. The practical values of β for capillary columns with four different internal diameters (0.25, 0.50, 1.00, 1.55 mm) relative to the film thickness (usually between 0.25 and 1.5 μm) vary between 50 and 1500. At the same temperature, the partition coefficient (K) is independent of the type of column being used. This is

because if β becomes larger (as in the case of a capillary column), k should become smaller according to the equation $K = \beta k$. As a consequence, the correct retention time (t^1R) depends only on the liquid phase, because if k becomes smaller, the "dead time" (t_M) should simultaneously become larger.

Since, at the same temperature and with the same partition liquid, the partition coefficient is independent of the type of column, the separation factor α also keeps the same value for both packed and capillary columns.

Equation (5) expresses the number of theoretical plates required to obtain the resolution (R) of two given peaks as a function of α and k. It is evident that if k becomes smaller while R and α are unchanged, n_{req} should increase.

Packed columns thus offer a better resolving power than capillary columns for the same plate number. In other words, in order to obtain the same level of resolution, a greater number of plates is needed when the chromatogram is carried out with the capillary column rather than with the packed column. /421

This is also apparent from equation (6): since β is larger for capillary columns while K and α remain unchanged, the last term to the right should increase.

Let us now consider capillary and packed columns with the same liquid phase and at the same temperature.

The number of theoretical plates needed to separate a given pair of components with either column can be calculated from equation (5). If we write the two pertinent equations and divide one by the other, the term $16[\alpha/(\alpha - 1)]^2$ can be eliminated, since,

at the same temperature, the relative retention should be the same for both columns. The resulting equation is[1]

$$\frac{n_T}{n_P} = \left(\frac{R_T}{R_P}\right)^2 \left(\frac{k_P}{k_T}\,\frac{k_T+1}{k_P+1}\right). \tag{11a}$$

If we simplify:

$$n_T = n_P F_1^2 F_2^2 \tag{11b}$$

where

$$F_1 = \frac{R_T}{R_P} \tag{12a}$$

$$F_2 = \frac{k_P}{k_T}\,\frac{k_T+1}{k_P+1}. \tag{12b}$$

Equation (12a) provides a factor relating the resolutions obtained with the two columns. If they are identical, F = 1 and

$$n_T = n_P F_2^2. \tag{13}$$

The factor F_2^2 shows that often more theoretical plates are required with capillary columns than with packed ones, in order to obtain the same resolution.

Another basic difference between capillary and packed columns is due to the fact that the latter are much less permeable to the carrier gas. A 100-m capillary column requires an operating pressure of 0.5-1.0 atm, while a packed column of the same length requires a much higher pressure (30-35 atm). The use of such high pressures obviously involves a series of practical problems for flow regulation and special devices for the introduction of the sample.

[1] The subscript T indicates tubular columns; P indicates packed columns.

6. Open Tubular Columns with Support

Open tubular columns with support (abbreviated as "SCOT columns") are the link between the known capillary columns with partition liquid coating the inside walls and the packed columns.

On the SCOT columns the filler, which is a thin film of the stationary phase deposited on a support of very fine diatomite (on the order of a micrometer), is deposited on the tube's walls. The surface area is thus increased by comparison with the open tubular columns, and thus the amount of stationary phase per unit length is also increased; the thin layer deposited on the column's walls is still there, and the tube is still "open." For this reason, it is possible to inject into the column relatively large amounts of substances, which makes trace analysis easier. Identification of effluents by mass or infrared spectrometry and sample collection are also made easier (0.4 ppm is the smallest amount detectable with an open tubular column with support, versus the 20 ppm detectable with a classical open tubular column).

7. Applications

Gases

Gas-solid gas chromatography is used in the analysis of mixtures of permanent gases or of vapors of very volatile substances, but with ingenuity it is possible to extend this field of application to include less volatile substances. The limited development of gas-solid chromatography relative to partition chromatography is due to the fact that traditional adsorbents, such as charcoal and silica gel have strongly curved adsorption isotherms. As a consequence, the elution peaks are strongly asymmetrical, with a steep front followed by a long tail; the retention times vary with the concentration and in particular they are very large with polar substances, causing a slow elution of

the components. In addition, under operational conditions, irreversible adsorption can take place; it can lead to deactivation of the adsorbent. Finally, while there are a great number of solvents for partition chromatography, there are very few active solids available: charcoal, silica gel, aluminum or molecular sieves.

Permanent Gases and Atmospheric Pollution

In spite of the disadvantages mentioned, gas-solid chromatography is indispensable in the separation of inorganic gases (permanent gases, rare gases, CO, CO_2, nitrogen oxides, etc.) and of gaseous hydrocarbons (CH_4, C_2H_4, C_2H_6, etc.) for which it is not possible to use partition liquids, due to the very low solubility.

Activated charcoal is used in analysis of permanent gases such as hydrogen, air (O_2 + N_2), carbon monoxide, nitrogen monoxide, /422 or methane, which may be separated at room temperature.

Alumina is used at 25°C for the separation of mixtures of volatile hydrocarbons (C_2H_6, C_2H_4, C_3H_8, etc.), in addition to carbon monoxide and carbon dioxide.

Silica gel at 25°C can be used for analysis of mixtures of light hydrocarbons and carbon dioxide [1].

Molecular sieves are the only adsorbents capable of separating hydrogen, oxygen, nitrogen, methane, and carbon monoxide at room temperature; however, they hold carbon dioxide irreversibly [2].

Argon, which is present in the atmosphere, is eluted together with oxygen; argon may be used as the carrier gas for the

determination of oxygen, or oxygen can be so used if argon is being determined. Separation of argon from oxygen can be obtained at a temperature of -72°C [3].

When hydrogen is used as the carrier gas on molecular sieves, a good separation of the noble gases is obtained in the order of their atomic weight: Ne, He (A + O_2), N_2, Kr, and Xe. In order to obtain better results, it is advantageous to use a programmed range of temperatures from room temperature to 110°C.

Complete resolution of noncondensable gas mixtures from motor vehicle exhausts is done with two columns: one with silica gel and one with molecular sieves. A device for two-column operation is installed in the gas chromatography apparatus; the sample is injected with the two columns in series. Since carbon monoxide is eluted by the molecular sieve column, this is excluded, and the other components are carried directly from the silica gel column to the detector.

Gas-solid chromatography will probably undergo substantial development, due to sensitization of public opinion to atmospheric pollution in urban and industrial areas. Many methods in this area have been developed in recent years, using highly sophisticated techniques and equipment.

Gas chromatography, especially after introduction of polyaromatic porous polymers as stationary phases, has some of the qualities required of a good analytical method: versatility, rapidity, use of small samples, and possibility of automation.

Until now, however, the sensitivity of the detectors was not sufficient to allow the use of small samples. An attempt to overcome this difficulty has been made by trapping the contaminants

contained in large gas volumes in refrigerated columns and later liberating them by heating. All the problems deriving from the need to preconcentrate the sample may be overcome if sufficiently sensitive detectors are available, capable of directly measuring the contaminants present in a very small air sample. The metastable helium detector has these characterstics of extreme sensitivity.

This detector has a high sensitivity, capable of measuring quantities on the order of one part in a billion.

Gaseous Hydrocarbons

Among condensable organic gases, hydrocarbons have received the most attention due to their industrial importance.

Alkanes and alkenes C_2-C_5 are usually separated using packed columns. The chromatography columns contain dimethylsulfolane and polyethylene glycol on a support or Chromosorb P 30-60 mesh as the partition liquids. They are made, respectively, of 4 m and 2 m of inox steel tubing (inside diameter 4.5 mm) [4]. The two columns used in series may, however, be replaced by a single column 6 m long. 1-Butene and isobutene are eluted together, but this pair can be separated in a long column containing dimethylsulfolane as the liquid phase (Fig. 1).

Complete separation can also be achieved with a 9-m column of benzyl cyanide and silver nitrate (cyanide 20% by weight, $AgNO_3$ 10%, on Firebrick C-22, 40-60 mesh).

Substances with Low Polarity: Hydrocarbons

Gas chromatography has been applied to the analysis of hydrocarbons in petrochemicals. James and Martin had already shown

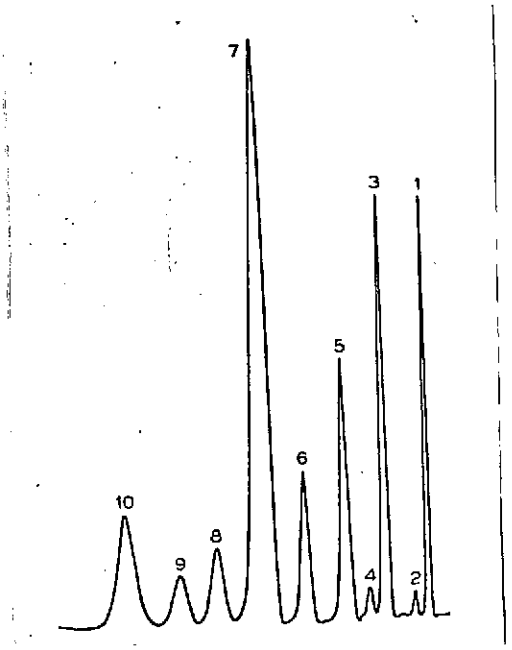

Fig. 1. Separation of C_1-C_5 alkanes and alkenes.
1) air + methane;
2) ethane + ethylene;
3. propane; 4. propylene;
5) isobutane; 6) butane;
7) isobutylene + 1-butene;
8) trans-2-butene;
9. cis-2- butene;
10) 1,3-butadiene.

the basic importance of the retention volume, i.e., that the individual hydrocarbon components should be identified by comparison of their retention volumes with two different types of liquid phases. They also examined the validity of alternate methods for identifying components of more /423
complex mixtures, using a sizable number of packed columns (6-4 m and 4 mm diameter) to isolated fractions of this type.

Since then, there has been a general trend to develop a column with a higher resolving power, operating efficiently only with very small samples. This involves serious difficulties if sufficient amounts of substances must be isolated for identification by other methods. Coated nylon and glass capillaries have, however, been used in these analyses [5, 6]. The majority of the individual paraffins contained in oil, up to C_8, have been identified using their relative retention volumes, which have been determined using pure reference compounds.

Paraffins

Straight-chain, cyclic and branched-chain paraffins are the main components of various petroleum products and are present in variable amounts.

Normal and branched paraffins are separated on nonpolar liquid phases according to their boiling point: branched-chain isomers are eluted before the corresponding n-paraffins with the same carbon number, usually after the lower normal paraffin. The liquid polar phases have little effect on the separation of n-paraffins from branched paraffins, and both types of hydrocarbons tend to be rapidly eluted from the above-mentioned phases. On nonpolar phases, the cycloparaffins (naphthenes) are slightly slowed down as compared with paraffins of similar boiling points; this effect becomes stronger on polar phases. Adsorbents retard normal and branched paraffins more than naphthenes, so that it is possible to separate paraffins from naphthenes of similar carbon numbers by coating an adsorbent with small amounts of liquid phase. This grouping of different paraffins according to their number of carbon atoms is useful in mass spectrometry analysis and whenever further separation can be carried out with a different type of liquid phase.

a) Pentanes

These four C_5-paraffin hydrocarbons -- 2,2-dimethylpropane, isopentane, n-pentane and cyclopentane -- have been separated using packed columns with a variety of liquid phases. Nonpolar phases such as n-hexadecane are adequate, but better separations are obtained with polar liquids, which are also used for the separation of gaseous hydrocarbons.

b) Hexanes

Hexanes and n-hexane have been separated using a squalane capillary column. Separation is more difficult and slower with a packed column; however, using a colum of squalane on Celite in series with a 40% content of isoquinoline on Celite, it has been /424 possible to shorten the analysis to about 40 min [7].

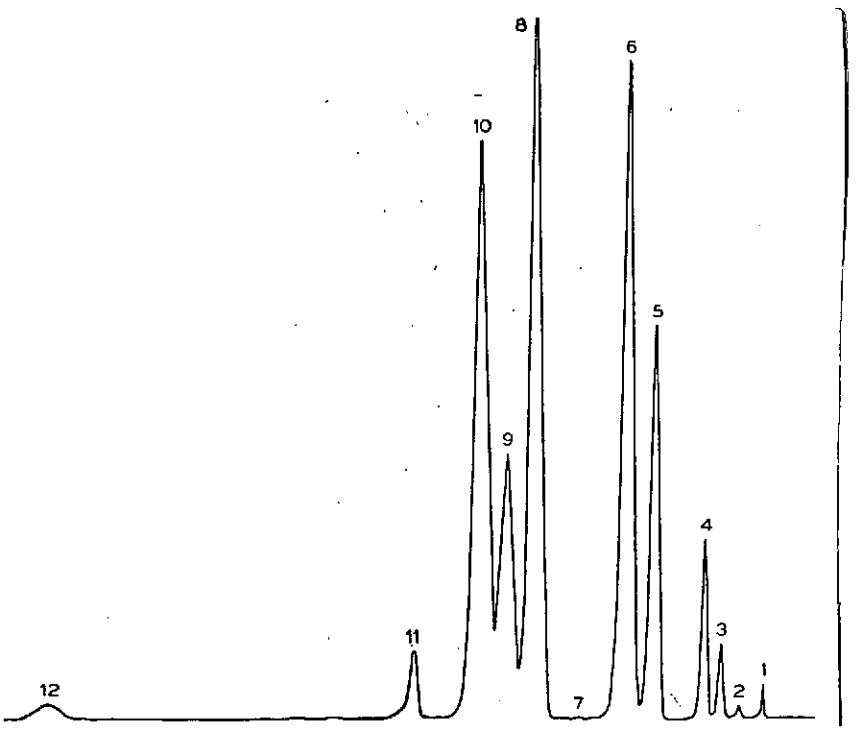

Fig. 2. Chromatogram of a DPL: 1) air; 2) propane; 3) isobutane; 4) n-butane; 5) isopentane; 6) pentane; 7) 2,2-dimethylbutane + cyclopentane; 8) 2,3-dimethylbutane + 2-methylpentane; 9) 3-methylpentane; 10) hexane; 11. methylcyclopentane; 12) benzene.

The duration of analysis can be reduced to less than 30 min for separation of hexanes and pentanes, together with cyclopentane, methylcyclopentane, cyclohexane, and benzene in a 6-m column containing dimethylsulfolane and polyethylene glycol on Chromosorb P (Fig. 2) [4]. Complete separation of all components present in light solvents of the hexane type and in gasolines (80-120 cuts) can be carried out with a hexadecane capillary column 150 m long. The complete analysis, up to o-xylene, takes place in about 120 min (Fig. 3) [8, 9].

c) Heptanes

A squalane capillary column 284 m long has been used at low temperatures for the separation of C_7 paraffins and naphthenes.

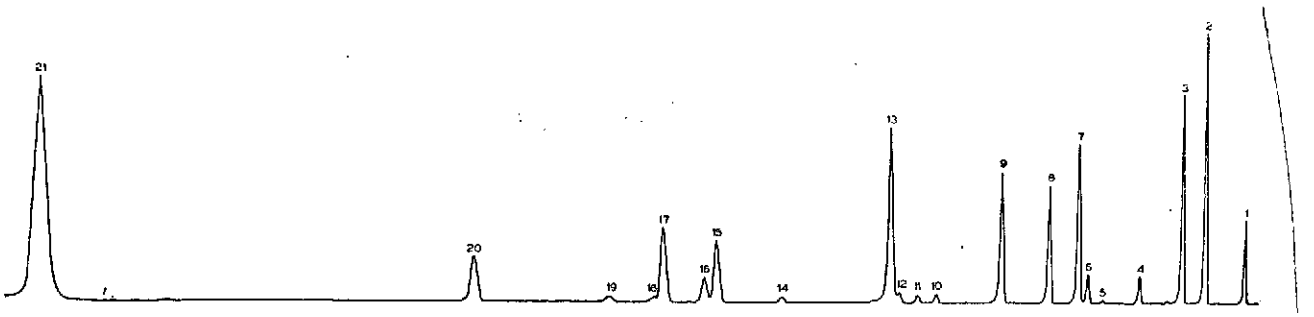

Fig. 3. Chromatogram of a light gasoline with a capillary column coated with hexadecane: 1) butane; 2) isopentane; 3) pentane; 4) 2,2-dimethylbutane; 5) cyclopentane; 6) 2,3-dimethylbutane; 7) 2-methylpentane; 8) 3-methylpentane; 9) hexane; 10) methylcyclopentane; 11) 2,3-dimethylpentane; 12) 2,4-dimethylpentane; 13) benzene; 14) cyclohexane; 15) 2-methylhexane; 16) 2,3-dimethylpentane; 17) 3-methylhexane; 18) 1-trans-3-dimethylcyclopentane + 1-trans-2-dimethylcyclopentane; 19) 3-ethylpentane; 20) heptane; 21) toluene.

If C_6 and C_8 paraffins are present, they come out between methylcyclopentane and 2,2-dimethylpentane, and also between methylcyclohexane and 2,2,3,3-tetramethylbutane [10].

For the separation of heptanes, the 150-m capillary column with hexadecane may also be used successfully at room temperature or at 40°C, if the mixture is not too complex and if the apparatus is provided with a refrigerated unit, in order to ensure reproducibility of retention times.

An analogous separation using packed columns would require the use of an 8-m column with 13% isoquinoline on Celite and of a 12-m column with 1-chloronaphthalene on Celite.

d) Octanes and Nonanes

The complexity of the oil fractions containing paraffin hydrocarbons C_8-C_9 is such as to cause considerable peak overlapping in gas chromatographic analysis. However, much useful information

has been obtained with C8-C9 paraffin compounds from oil alkylates using packed and capillary partition columns jointly with mass spectrometry [11].

e) High Molecular Weight Paraffins

The analysis of oil fractions with boiling points above 150°C is difficult because of the high number of isomers.

The determination of various groups of hydrocarbons present in these fractions is generally of greater interest than the separation of the individual components, so gas chromatography and spectrography are the most suitable techniques for this type of analysis. Straight-chain alkanes are an important group of hydrocarbons that may readily be determined with the combined use of gas chromatography and an extraction procedure with molecular sieves. This method has been applied to oil fractions in the C_5-C_{50} range, and results have been obtained for total and individual n-alkanes [12].

Another method has been developed for the determination of n-paraffins in heavy diesel oils. The method uses the formation of urea adducts in order to isolate n-paraffins, which are then analyzed with good resolution by gas-liquid chromatography.

Solid paraffins containing predominantly C_{20}-C_{40} n-alkanes can be characterized by gas-liquid chromatograms obtained by separation in short packed columns at temperatures around 280°C [13].

Olefins

Olefins derived from various oil processes are extremely complex mixtures. Gas chromatography has been used recently in the analysis of their components.

On liquid nonpolar phases, olefins are largely separated according to their boiling points. Numerous changes occur on liquid polar phases, since the elution rate is more affected by the position and number of the double bonds in the molecule.

For example, good separation of C_2-C_7 alkenes has been carried out with a 91-m capillary column coated with silicone liquid [4]. The same column was used to separate 25 olefins present in a commercial heptane sample.

In the fractions coming from catalytic cracking there are many isomeric olefins. Analysis of the C_5-C_6 olefins present in these fractions, which contain monoolefins, cycloolefines, and dienes, requires the use of five different columns [15]. The first column contains a modified adsorbent, graphite-carbon coated with dimethylsulfolane, diisodecyl phthalate, β,β'-oxydipropionitrile and squalane. /425

Another method, applied to the analysis of C_7-C_8 monoolefins, is based on the identification and determination of paraffins corresponding to the various isomeric olefins by comparison of the chromatograms before and after hydrogenation [16]. In columns containing liquid polar phases, olefins tend to be slowed relative to the corresponding paraffins.

Aromatics

A sizable number of aromatic compounds has been determined by chromatography. The C_6-C_9 aromatics are especially important in industry, and their separation with packed columns of different polarities (e.g. containing liquid paraffins, dioctyl phthalate, and polypropylene glycol) has been reported in the literature [17]. The polar phases separate aromatics from paraffins in the same boiling range, since the latter are rapidly eluted due to their

low solubility; on polyethylene glycol, for example, benzene (b.p. 80°C) is eluted after the C_{10} paraffins (b.p. 170°C) [18]. Liquid phases of this type have been used to determined aromatics in aviation gasolines [19]. The saturates and the total aromatics are now determined in cracking gasoline: the saturates and the olefins are completely separated from the aromatics in a column containing β,β'-thiodipropionitrile on Firebrick and the olefins are removed at the end of the column with mercury perchlorate, so that when the gas flow is inverted, the saturated hydrocarbons are recorded in a single peak. The results obtained by this method are in agreement with those obtained by liquid chromatography and mass spectrometry.

The separation of m- and p-xylene has presented serious difficulties, but 7,8-benzoquinoline (in a 15-m capillary column at 79°C) has efficiently solved this problem by separating these isomers and o-xylene and ethylbenzene as well [20].

Tetrahalophthalate ester is recommended as the liquid phase for the separation of aromatics, and m- and p-xylenes are especially well resolved in a 9-m packed column. The elution sequence is m-xylene and p-xylene, the opposite of what happens with benzoquinoline.

The aromatic cuts are also analyzed using a column with Apiezon L (2 m at 106°C). The various compounds up to hydrindene are separated in less than 30 min (Fig. 4). Isomeric xylenes are separated in a column with isodecyl phthalate on Bentone (Fig. 5).

This procedure has been developed in an attempt to find substantial, continuous differences in the composition of aromatic solvents derived from coal distillation and from oil fractions. This problem has considerable industrial importance, since the customs rate differs according to the source. Analyses performed

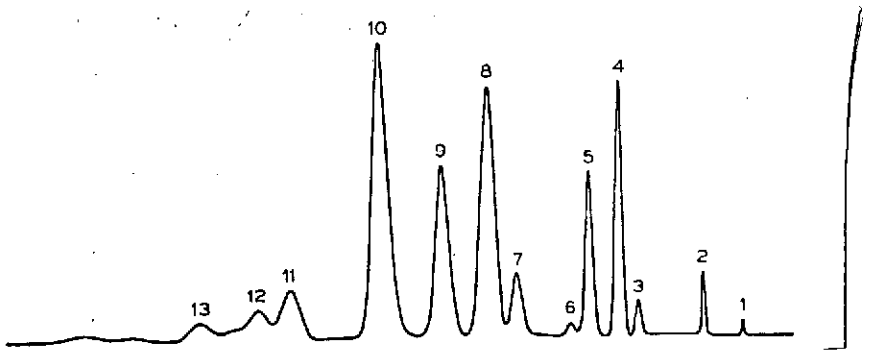

Fig. 4. Chromatogram of an aromatic solvent on Apiezon L: 1) benzene; 2) toluene; 3) ethylbenzene; 4) m,p-xylene; 5) o-xylene; 6) isopropylbenzene; 7) propylbenzene; 8) 1-methyl-3-ethylbenzene + + 1-methyl-4-ethylbenzene; 9) 1-methyl-2-ethylbenzene + + 1,3,5-trimethylbenzene; 10) 1,2,4-trimethylbenzene; 11) 1,2,3-trimethylbenzene; 12) hydrindene; 13) C_{10}.

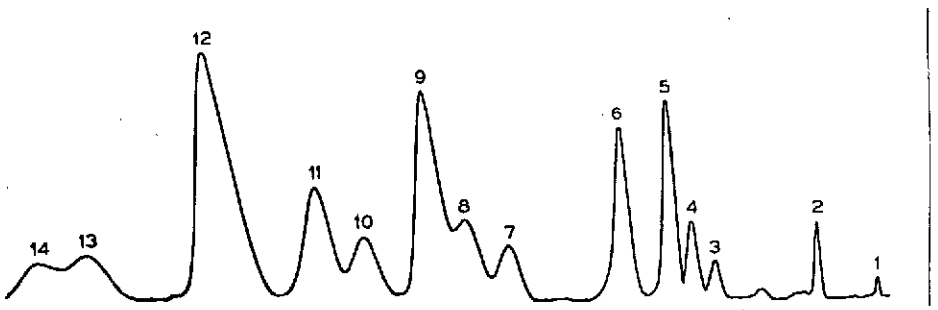

Fig. 5. Chromatogram of an aromatic solvent on Bentone 34: 1) benzene; 2) toluene; 3) ethylbenzene; 4) p-xylene; 5) m-xylene; 6) o-xylene; 7) propylbenzene; 8) 1-methyl-4-ethylbenzene; 9) 1-methyl-3-ethylbenzene; 10) 1-methyl-2-ethylbenzene; 11) 1,3,5-trimethylbenzene; 12) 1,2,4-trimethylbenzene; 13) 1,2,3-trimethylbenzene; 14) hydrindene.

on various solvents have shown considerable differences depending on origin. The hydrindene perctange is much higher in solvents deriving from coal. In addition, certain ratios of 1-methyl/ /2-ethyl/1,3,5-trimethylbenzene; isopropylbenzene/n-propylbenzene vary distinctly in the two cases.

The separation and analysis of C_6-C_{10} aromatic hydrocarbons, even in the presence of saturated C_1-C_{11} hydrocarbons, may be carried out in a single 100-m capillary column coated with TCEP (1,2,3-tris-2-cyanoethoxypropane). The column temperature is kept at 50°C for 4 min after introduction and is programmed at 5°C/min up to 90°C. The analysis is carried out in about 40 min. It was previously necessary to first separate the aromatics from /426 the paraffins and the naphthenes, and only then separate the various aromatic components.

The high molecular weight aromatics such as alkylbenzenes C_{12}-C_{26} are separated on columns containing an asphalt on Firebrick at temperatures between 240 and 320°C or on a short column of 5% Apiezon L on Celite.

The separation of alkyl diphenyls has been carried out on a column containing Apiezon M at 197°C. It has been observed that ortho-substituted compounds are eluted more rapidly than the meta- and para-substituted ones, due to the steric effect resulting from ortho-substitution.

Gas chromatography techniques for analysis and identification of aromatic polynuclear hydrocarbons have been applied to the examination of atmospheric dust from various polluted areas. Through extraction with appropriate solvents of different polarities, it is possible to isolate from the dust a fraction consisting predominantly of a mixture of polynuclear hydrocarbons, which is then examined by gas chromatography with separation of the various components using fixed phases, such as SE 30, SE 52, XE 80, and using high-efficiency packed or capillary columns.

Gas chromatography has also been applied to the analysis of oils and anthracene pastes.

The components of the "pastes" are separated at programmed temperatures (1°C/min from 135° to 225°) using a column of SE 52 6 m [21].

Asphalts

Petroleum asphalts have high boiling points; they are so complex that their separation by gas chromatography is impossible. However, a clever inversion of gas chromatography does make it possible to obtain a fast characterization of these rather intractable materials. The method consists of using an asphalt of unknown composition as the stationary phase on a solid support, characterizing it by measuring the retention volumes of a series of selected compounds with different functional groups [22, 23, 24, 25].

Lead Antiknock Compounds

The determination of lead antiknock additives in fuels has considerable practical importance. Gas chromatography permits separation of the various lead compounds, which, with the use of an electron capture device, has a high sensitivity. A fast chromatographic method [26, 27, 28] carries out the separation with a 3 m x 1/8" column of 10% 1,2,3-tris-(2-cyanoethoxy)-propane (TCEP) on Chromosorb W-HMDS 80/100 followed by an aftercolumn with $AgNO_3$ to stop the additives (ethylene chloride and bromide) which are not to be determined and which interefere with the analysis. The accuracy of this method has been estimated by the authors to be about 4%.

Electron capture, although sensitive, is unfortunately not sufficiently specific and is not even a very sensitive detection method. It requires extreme attention and cleanliness, and microchemical techniques must be stricted followed.

Gas chromatography and atomic absorption have been combined for the solution of a series of difficult problems which could not be solved using other methods.

Several laboratories use the specificity of atomic absorption for individual inorganic elements and the separation power of gas chromatography to differentiate and determine organo-metallic compounds with similar chemical compositions.

Alternately, with gas chromatography it is possible to separate the components of a gasoline sample and introduce them individually in the burner for atomic absorption. The atomic absorption spectrophotometer, adjusted for lead determination, records a peak for each lead-alkyl emitted by the gas chromatography apparatus. The procedure is standardized using mixtures of known composition. The samples of gasoline are usually 1 µl, and up to 20 µg of lead as lead-alkyl can be detected.

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